

Predictions of the Electronic Structure and Related Properties of Cubic Calcium Hexaboride (CaB_6)

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Abstract

We present theoretical calculations of the electronic structure and related properties of calcium hexaboride (CaB_6) in the zinc-blende structure. Our nonrelativistic calculations employed a local density functional approximation (LDA) potential and the linear combination of atomic orbitals (LCAO) formalism that implemented the *ab initio* Bagayoko, Zhao, and Williams (BZW) method (Bagayoko et. al 1999). The BZW procedure *avoids* a recently identified spurious effect. This effect, inherent to the use of basis sets in variational calculations, has plagued ab-initio calculations of electronic properties of semiconductors since their inception. Unlike previous calculations, there is an agreement between our findings and experimental results. In particular, our implementation of the *ab initio* BZW method led to a calculated, direct, band gap of 0.87 eV for CaB_6 at the X point. The BZW procedure has so far been unfailingly successful in reproducing or predicting the correct band gaps of semiconductors using density functional potentials. Key words: *calcium hexaboride, density functional theory, electronic structure, band gap, semiconductor, BZW method*

I. INTRODUCTION

The anomalous physical properties of metal hexaborides have been of great interests to researchers in the past several years. Specifically, the uncharacteristic behavior of divalent calcium hexaboride (CaB_6) has led to much controversy among researchers to obtain and understand the correct theoretical and/or experimental band gap (E_g) value for CaB_6 . (Souma and Takahashi 2007, Lee and Wang 2005, Denlinger et al. 2002, Souma et al. 2004, Wu et al. 2004, Kino et al. 2002, Tromp et al. 2001, Hasegawa and Yanase 1979). As such, researchers have reported theoretical band gap values which suggest that CaB_6 may be a semi-metal or a semiconductor. The simple cubic structure of CaB_6 is comprised of metal Ca atoms (Ca) located at the corners and boron (B) octahedral cages at the center that are interconnected by covalent B-B bonds. Some reported, theoretical band gap (E_g) values for CaB_6 range from 0.3 – 1.27 eV at the X high symmetry point. The discrepancies which exist among the theoretical band gap values have been attributed to the utilization of different approximation methods (i.e., local density approximation (LDA), screened-exchange local density approximation (LDA) [sX-LDA], generalized gradient approximation (GGA), muffin-tin approximation (MTA), warped muffin-tin approximation (WMTA), weighted density approximation (WDA), and Green's function (G) and dynamically screened Coulomb interaction (W) approximation [GWA]). We calculated the electronic band structure of CaB_6 using an LDA potential, the linear combination of atomic orbitals (LCAO) formalism, and the *ab-initio* BZW method. Our results show that calcium hexaboride is a semiconductor with a calculated band gap of 0.87 eV, which is in excellent agreement with experimental values. Until recently (G. L. Zhao et al. 1999, Bagayoko et al. 1998, Williams 1998), LDA calculations for semiconductors often led to band gaps that are typically 30-50 % smaller than the experimental values (Rubio et al. 1993, Vogel et al. 1997). The discrepancies between LDA and experimental results have been ascribed to limitations of the local-density approximation.

Lee and Wang (2005) performed ab-initio total energy calculations with LDA and sX-LDA potentials. Their findings indicated that CaB_6 behaved as a semi-metal with zero to negative band gaps, i.e., the conduction band minimum (CBM) and valence band maximum (VBM) at the X-point, with LDA calculations, either overlap or the former is lower than the latter. sX-LDA calculations led to a rather large band gap of 1.27 eV for CaB_6 . Tromp et al. (2001) performed pseudopotential calculations with LDA and GWA potentials and also observed both the semi-metallic and semiconductor characteristics for this material, respectively. Their GWA calculations produced a gap of 0.8 ± 0.1 eV. Wu et al. (2004) also calculated a gap of 0.8 eV with Plane Wave (PW) calculations and in the weighted density approximation (WDA). Massidda et al. (1997) utilized an LDA potential and Rodriguez et al. (2000) employed a generalized gradient approximation (GGA) potential in their calculations. The latter group implemented the full potential linearized augmented plane wave (FLAPW) method. Massidda et al. and Rodriguez et al. both reported a semi-metallic band structure for CaB_6 . Hasegawa and Yanase (1979) performed augmented plane wave (APW) calculations, within the muffin-tin formalism, and they obtained a zero band gap. They subsequently utilized the warped muffin-tin (WMTA) and found a band gap of 0.3 eV. They attributed the small or zero band gaps to a strong hybridization of the B sp states with the Ca d states around the Fermi level.

Experimental measurements of the electronic structure of calcium hexaboride have been reported by Souma and Takahashi (2007), Souma et al. (2004), and Denlinger et al. (2002). They both utilized the high-resolution angle-resolved photoemission spectroscopy (ARPES) technique and reported experimental band gaps of 1.0 eV. Both groups suggested that CaB_6 is intrinsically a semiconducting material.

Recently, Bagayoko and co-workers identified a basis set and variational effect inherently associated with the use of the linear combination of atomic orbital (LCAO) formalism in variational calculations of the Rayleigh-Ritz type (Bagayoko et al. 1998, Zhao et al. 1999, Bagayoko and Franklin 2004). Specifically, the effect consists of a possible lowering of some unoccupied energy levels or bands

for molecules, clusters, or solids on account of a mathematical artifact (Bagayoko et al. 1998). *This artifact consists of any lowering of unoccupied energy levels, upon increases of the size of the basis set, when the occupied energy levels do not change.* This situation stems from the Rayleigh theorem (Bagayoko 1983) that simply states: a given variational eigenvalue, upon an increase of the size of the basis set, is never increased; either it remains unchanged (i.e., if it is equal to the corresponding exact eigenvalue of the matrix) or it is lowered to approach the exact eigenvalue from above. Clearly, upon increases of the size of the basis set, occupied and unoccupied eigenvalues tend to be lowered to approach their corresponding exact values. As long as at least one occupied eigenvalue changes, a lowering of an unoccupied eigenvalue is ascribed to changes in the Hamiltonian which is constructed using only the wave functions of the occupied states. If, however, no occupied energy level changes from one self-consistent calculation to the next (with a larger basis set), then any lowering of an unoccupied level is not due to changes in the Hamiltonian but rather to a direct consequence of the Rayleigh theorem.

Several different methods, which employed different approximation potentials, have been utilized to obtain the electronic structure of CaB_6 . The above discrepancies between calculated and measured values of the band gap of CaB_6 are a key motivation for this work. It is our contention that these discrepancies are due to the fact that researchers have not avoided the spurious basis set and variational identified by Bagayoko et al. (1998, 2007) in their calculations of the band structure for CaB_6 . Hence, a key motivation for this work is the resolution of the disagreements noted above between theoretical values, on the one hand, and the experimental band gaps (i.e., 1.0 eV), on the other, for CaB_6 . We describe below the general and distinctive features of our method, with the distinctive one consisting of our implementation of the BZW procedure that avoids the spurious effect associated with the Rayleigh theorem. This description is followed with our findings for the electronic properties of calcium hexaboride, including the band gap.

II. METHOD

A. General approach: LDA potential and LCAO

Our calculations utilized an expanded version of the electronic structure calculation program package from the Ames Laboratory of the Department of Energy (DOE) in Iowa (Ching 1990, Feibelman et al. 1979, Harmon et al. 1982, Zhao et al. 1989, Zhao and Harmon 1992, Ching et al. 1987). Details of the computational method are available the publications just cited above. We employed the Ceperley-Alder (Ceperley and Alder 1980) local density functional potentials as parametrized by Perdew and Zunger (1981). We implemented the linear combination of atomic orbital (LCAO) formalism. In doing so, we utilized Gaussian functions. We discuss below our unique implementation of the LCAO formalism in accordance with the Bagayoko, Zhao, and Williams (BZW) method.

B. The BZW Method

In *ab-initio*, self-consistent calculations that employ the LCAO method, electronic eigenfunctions are expanded using basis sets derived from atomic calculations (Bagayoko et al. 1996, Dean et al. 1980). Charge densities and potentials are constructed using the wave functions of *occupied* states. The Hamiltonian matrix is generated and diagonalized. The key output quantities are energy levels or bands and related wave functions. The resulting output wave functions, for the *occupied* states only, are employed to generate a new charge density and to construct the Hamiltonian and the computations are repeated in an iterative process until self-consistency is reached. Various measures are utilized to define self-consistency; i.e., when basic quantities, such as charge densities, potentials, eigenenergies, etc., are unchanged from one iteration to the next.

The BZW method requires suggests a minimum of three self-consistent calculations that utilize basis sets of different sizes. It generally begins with the minimum basis set, i.e., the one just large enough to account for all the electrons of the atomic or ionic species that are present in a molecule, a cluster, or a

solid (in this case, CaB_6). Completely self-consistent calculations are performed with this minimum basis set. For the second calculation, the minimal basis set is augmented with one or more atomic orbitals that belong to the unoccupied, lowest-lying energy levels in the atomic or ionic species. After the iterations to self-consistency, the self-consistent *occupied* energies from calculations I and II are compared, graphically and numerically. They are usually different. Successive, self-consistent calculations are carried out with an increasingly large basis sets that are methodically augmented as done after the first one. The basis set for each calculation include the one for the one preceding it plus orbitals representing the next, unoccupied, energy level in the atomic or ionic species in the solid. We always compared the occupied energies level from a calculations to those of the immediately preceding it. This process continued the occupied energy levels of Calculation N were found to be identical to those of Calculation (N+1), within computational errors. When this coincidence occurred, we selected the outputs of Calculation N, with the smaller basis set, to describe the electronic and related properties of calcium hexaboride. The outputs of Calculation (N+1) are not selected due to the fact that the occupied energies from this calculation are the same as those from Calculation N, even though some of the unoccupied energies are lowered on account of the Rayleigh theorem (and not a change in the Physics, i.e., the ground state Hamiltonian). The basis set for the selected calculation is referred to as the optimal basis set, i.e., one that is large enough to ensure completeness vis à vis the description of the ground state but not so large as to cause unphysical lowering of some unoccupied energy levels.

C. Computational Details

Divalent CaB_6 has a simple cubic structure with a Cesium Chloride (CsCl) type lattice arrangement. It is a member of the $O_h^1(Pm3m)$ space group. Our calculations utilized a zero temperature lattice constant of $a = 7.83291$ a.u. (4.1450 \AA) and internal parameter $u = 0.207$. The atomic wavefunctions of the neutral states of Ca and B were obtained from self-consistent *ab initio* atomic calculations. The radial parts of the

atomic wave functions were expanded in terms of Gaussian functions. A set of even-tempered Gaussian exponentials was employed for Ca with a minimum of 1.0×10^{-1} and a maximum of 1.2×10^4 and for B with a minimum of 1.2×10^{-1} and a maximum of 5.0×10^4 . We used 17 Gaussian functions for the s and p states and 15 for the d states for Ca. For B, we utilized 16 Gaussian functions for the s and p states and 14 for the d states. A mesh of 10 k points, with proper weights in the irreducible Brillouin zone, was employed in the self-consistent iterations. The high symmetry points utilized in the simple cubic (sc) Brillouin zone are M, Γ , X, M, R, X, and Γ . The positions for the high symmetry points are $M = \frac{\pi}{a}(1,1,0)$, $\Gamma = (0,0,0)$, $X = \frac{\pi}{a}(1,0,0)$, and $R = \frac{\pi}{a}(1,1,1)$. Upon reaching self-consistency, the error made in accounting for 28 electrons was -0.02906599. The self-consistent potentials converged to a difference around 10^{-5} after about 60 iterations. The total number of iterations varied with the input potentials.

III. RESULTS

We performed three (3) self-consistent neutral calculations in order to determine the optimal basis set as per the *ab initio* BZW procedure. Table I shows the basis set composition for all three neutral self-consistent calculations. The calculation of the electronic energy bands first consisted of carrying out completely self-consistent calculations for CaB_6 using a minimal LCAO basis set. The initial charge density for CaB_6 was calculated using the atomic orbitals of Ca (1s2s2p, 3s3p4s) and B (1s2s, 2p). We then repeated the self-consistent calculation using the above minimal basis set as augmented by the orbitals describing the lowest-lying, unoccupied energy levels (of Ca or B). Hence, Ca (3d⁰) orbitals were added to the minimal basis set, where the superscript index of zero indicates that these states are unoccupied in the free atoms. We then plotted the self-consistent energy bands from these two distinct calculations, i.e., calculation I and calculation II, and compared the *occupied bands* numerically and graphically. Differences were observable. We then performed calculation III and compared its results to those of calculation II, as

shown in Figure 1. Within the uncertainties associated with our computations, the occupied energies from Calculations II and III are approximately the same. Although the occupied bands are not perfectly superimposed, there exist no differences in their shapes and branching. As per the BZW method, the outputs of Calculation II provide the description of the electronic and related properties of CaB_6 . Please note however that this determination is made based on the convergence of the occupied energies vis à vis a variation of the size of the basis set. Figure 1 clearly shows drastic changes in the unoccupied energies of Calculation III as compared to those from Calculation II.

Our calculated band gap for CaB_6 is 0.87 eV, in good agreement with the experimental value of 1.0 eV. This agreement is particularly significant in light of the previous, negative or very small (i.e., 0.3 eV) theoretical values for this band gap as summarized in Table II. The results reported in this table clearly show that, with applicable uncertainties, the results of our Calculation II agree with the experimental measurements reported by Souma and Takahashi (2007) and Denlinger et al. (2002). Our calculated, electronic eigenvalues at high symmetry points, provided in Table II, are expected to allow further comparison with future experimental results.

IV. CONCLUSION

By utilizing the *ab-initio* BZW method, we calculated the electronic structure of calcium hexaboride. Unlike previous theoretical studies, we obtained a band gap of 0.87 eV that is in good agreement with experiment. This result is further indication of the reliability of the Bagayoko, Zhao and Williams (BZW) method in correctly describing electronic properties of semiconductors within density functional theory, in general, and the local density approximation, in particular. Future measurements on CaB_6 are expected to confirm the accuracy of the band energies in Table III.

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Table 1. Basis Sets for Calculations I to III

Orbitals added to the minimal basis set (basis set I) are in bold.

Basis Set #	Calcium CORE	Calcium VALENCE	Boron CORE	Boron VALENCE
I	$1s^2 2s^2 2p^6$	$3s^2 3p^6 4s^2$	$1s^2$	$2s^2 2p^1$
II	$1s^2 2s^2 2p^6$	$3s^2 3p^6 4s^2$ $3d^0$	$1s^2$	$2s^2 2p^1$
III	$1s^2 2s^2 2p^6$	$3s^2 3p^6 4s^2$ $3d^0 4p^0$	$1s^2$	$2s^2 2p^1$

**Table 2. Comparison of Theoretical (Calculated) and Experimental
Band Gaps of Cubic Calcium Hexaboride (CaB₆)**

Authors	Band Gap E _g (eV)	Method	Potential*
Theoretical Results			
Lee and Wang 2005	1.27 eV	Ab-initio total energy	sX-LDA
	Negative gap	Ab-initio total energy	LDA
Tromp et. al 2001	0.8 ± 0.1 eV	Pseudopotential	GWA
	Negative gap	Pseudopotential	LDA
Wu et. al 2004	0.8 eV	Plane Wave (PW)	WDA
Massidda et. al 1997	Negative gap	Full Potential Augmented Plane Wave (FLAPW)	LDA
Rodriguez et. al 2000	Negative gap	Full Potential Augmented Plane Wave (FLAPW)	GGA
This work	0.87 eV	Linear Combination of Atomic Orbitals (LCAO)	LDA-BZW
Hasegawa and Yanase 1979	0.3 eV	Augmented Plane Wave (APW)	WMTA
	Negative gap	Augmented Plane Wave (APW)	MTA
Experimental results			
Souma and Takahashi 2007	1.0 eV	Angle-Resolved Photoemission Spectroscopy (ARPES)	N/A
Souma et. al 2004	1.0 eV	Angle-Resolved Photoemission Spectroscopy (ARPES)	N/A
Denlinger et. al 2002	1.0 eV	Angle-Resolved Photoemission Spectroscopy (ARPES)	N/A

*The potentials utilized for the above theoretical calculations are as follows:

screened-exchange local density approximation (LDA) [sX-LDA], local density approximation (LDA), generalized gradient approximation (GGA), muffin-tin approximation (MTA), warped muffin-tin approximation (WMTA), weighted density approximation (WDA), and Green's function (G) and dynamically screened Coulomb interaction (W) approximation [GWA]

Table 3. LDA-BZW Calculated Eigenvalues (eV) of Cubic Calcium Hexaboride (CaB_6), at High Symmetry Points in the Brillouin Zone. The Fermi energy -4.9326 eV is set equal to zero in this table.

$a = 4.1450 \text{ \AA}$ and $u = 0.207$
Band Gap = -0.87 eV

M	Γ	X	R
-15.5512	-15.7939	-15.6238	-15.432
-8.09681	-6.59419	-8.7352	-8.02797
-7.98416	-6.52697	-6.32506	-7.83014
-5.88913	-6.50684	-6.31636	-7.71258
-5.06109	-6.4965	-5.66926	-3.74023
-4.01616	-4.16909	-3.74432	-3.62758
-2.14618	-3.81425	-1.81447	-3.44635
-2.01529	-0.26939	-1.71243	-1.51433
-1.32031	-0.20436	-1.33282	-1.2365
-1.11976	-0.09878	0	-1.05336
4.7106	3.893708	0.866962	5.325582
4.743254	3.956567	3.762548	5.377284
4.75305	4.065141	3.859965	5.390346
5.082311	4.121197	4.592502	5.474974
5.096188	4.147592	4.712505	5.48096
5.73675	5.209389	5.383815	5.528853
5.77158	5.257825	7.251347	8.484033

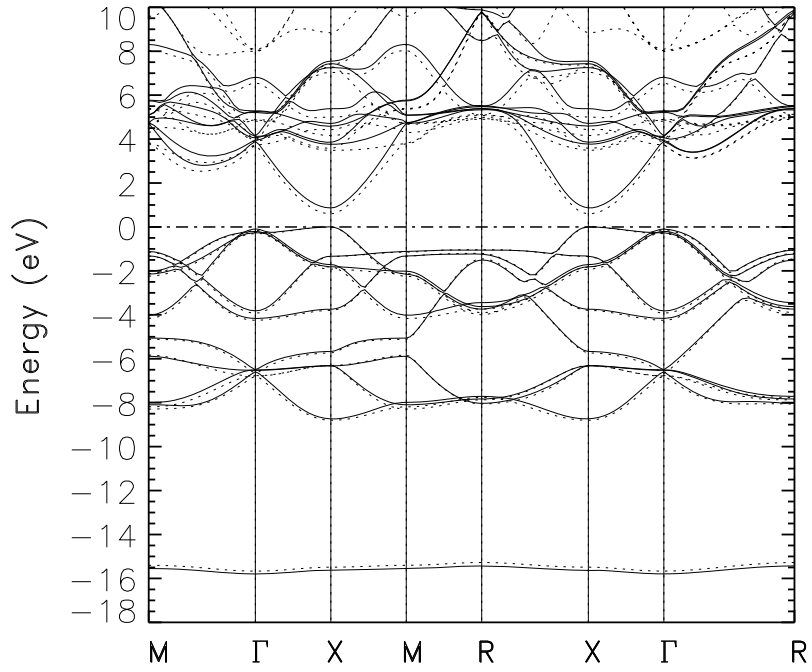


Fig 1. LDA-BZW band structure of cubic calcium hexaboride (CaB₆) resulting from Calculation II(—) and Calculation III(-----), *with the Fermi levels from the two calculations superimposed.*

The band gap is 0.87 eV and our optimal basis set is Calculation II.

